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Characterization of Naturally Grown Oxide Layers on Copper with and without Benzotriazole by Electrochemical and Photoelectrochemical Measurements

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Abstract

The active corrosion of ancient artefacts (bronze disease) is linked to the presence of copper chloride underneath Cu(I) oxide formed at the surface of bronze. The properties of the Cu(I) oxide determine the mechanism of formation of the corrosion layer and their knowledge would to develop efficient stabilization treatments.

The aim of our work is to characterize the structure and the electronic properties of Cu(I) oxide layers formed in different conditions (atmospheric and aqueous electrolyte) under open-circuit potential, using electrochemical and photoelectrochemical methods and SEM. Photoelectrochemistry allows the characterization the semiconducting properties of the passive layer and leads to a better knowledge of the nature of the electrode/solution interface and of the electrochemical reactions occurring at the oxide surface. Atmospheric Cu(I) oxide shows mainly p-type behaviour, whereas Cu(I) oxide layers formed at open-circuit potential by immersion in a NaCl solution were shown to exhibit p-type behaviour during the first hours of immersion and simultaneous n-p behaviour for longer immersion times.

In the presence of benzotriazole added to the sodium chloride solution, the photoelectrochemical measurements revealed modifications of the semi-conducting properties of the Cu_2O layer (duplex p-n layer from short immersion times) and showed that BTA makes the oxide layer more insulating. Results will be discussed in regards to the Cu(I) oxide role on the bronze disease.

Introduction

The active corrosion of ancient artefacts made of copper or copper-tin alloys is correlated with the presence of copper chloride species in the corrosion layer between the top Cu(I) oxide layer and the copper/ oxide interface. The mechanism of formation of such a structure is yet not well understood and seems even contradictory with the mechanism of formation of the corrosion layer on copper in a chloride containing electrolyte. Indeed, at the open circuit potential (*i.e.* corrosion potential), only Cu(I) oxide is observed during the first hours of immersion in a NaCl solution, as shown by XPS analysis [1]. For a longer period of immersion (3 days immersion in a 0.5M solution), the basic cupric hydroxychloride layer is already formed, but on the top of the Cu_2O underlayer. Consequently, the presence of copper-chloride at the metal/oxide interface supposes that chloride ions are able to diffuse through the copper oxide layer, either by ionic diffusion through the oxide, or by migration through the cracks or the pores of the layer [2]. A fundamental understanding of the structure and the conducting properties of the Cu(l) oxide would allow a better control of the layer against corrosion. The aim of our work is to characterize the structure and the electronic properties of Cu(I) oxide layers formed in different conditions in aqueous 0.5M NaCl at the open circuit potential, using electrochemical, photoelectrochemical methods and Scanning Electron Microscopy (SEM).

Experimental

The experimental devices for electrochemical and photoelectrochemical experiments are described in references [3] and [4]. All the copper electrodes were mechanically polished (grade 1000), rinsed in deionized water and air dried before immersion in an air saturated electrolyte (NaCl 0.5M) at the open-circuit potential. Prior to the electrochemical reduction of the layers, deaeration was achieved by bubbling nitrogen gas through the solution. All the potentiodynamic reduction plots of Cu_2O layers formed on the copper surface were performed at a potential scanning rate of 10 mV/s.

A scanning electronic microscope equipped with a X-ray analyser (Energy Dispersive Spectrometry) was used. The oxygen amount was semi-quantitatively determined using an ultra-thin window.

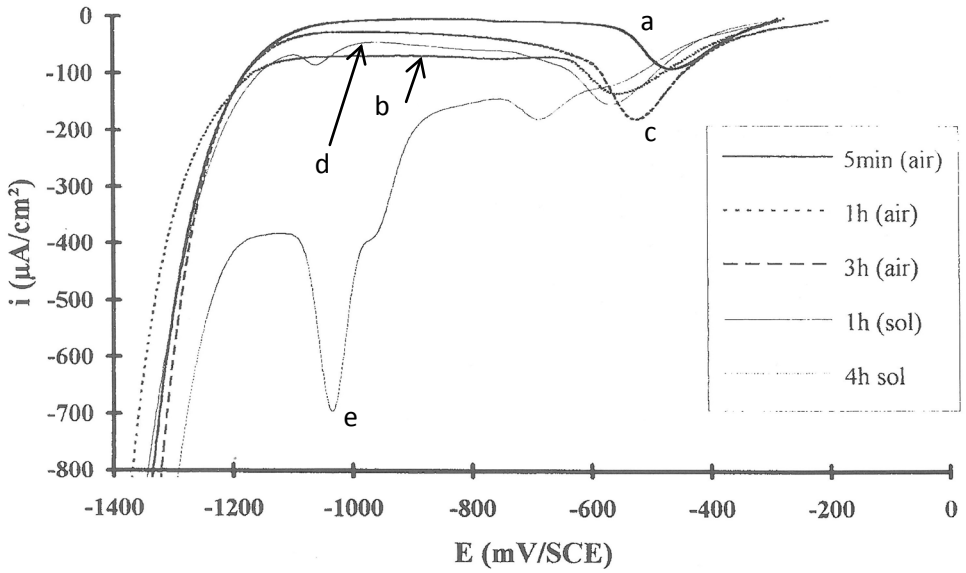

Figure 1. Electrochemical reduction of Cu(I) oxide layers formed after different air exposure times: **curve a** (5 min), **curve b** (1h), **curve c** (3h); or in an aerated 0.5M sodium chloride solution after different immersion times: **curve d** (1h), **curve e** (4h). Scanning rate: 10 mV s^{-1}

Results and Discussion

Electrochemical Behaviour

From the results of the literature [5-7], it appears that the electrochemical behaviour of a Cu(I) oxide layer on copper critically depends on the film preparation conditions (nature of the electrolyte, surface preparation prior to immersion, etc). In a NaCl aqueous solution, generally one or several reduction peaks can be observed in a wide potential range from -0.4 to -1.2 V/SCE. The first peak is relative to the most reactive Cu(I) oxide layer. This layer is formed during air exposure, before immersion, and appears between -450 and -600 mV/SCE in a 0.5M NaCl solution. Important modifications of the reduction peak values occur as a function of the atmospheric exposure time of the copper sample, prior to the electrochemical reduction. (Figure 1: curves a, b, c). These modifications can be correlated mostly with the oxide film thickening.

The second peak corresponds to an oxide layer grown in a 0.5M NaCl aqueous solution by immersion of the copper sample after surface polishing. This oxide layer is reduced at more cathodic potentials than the atmospheric one, thus showing a better stability. A displacement of the reduction peak towards more negative potentials, observed with increasing immersion times, is not only the result of the thickening of the film, but also of successive modifications of the oxide structure. The latter occurs during the formation of the layer 1 (Figure 1; curves d, e).

The inhibiting effect of BTA, added to the NaCl solution, leads to further modifications in the electrochemical behaviour of Cu_2O. As a consequence of the ability of BTA to stabilize the Cu_2O layer (Figure 2),

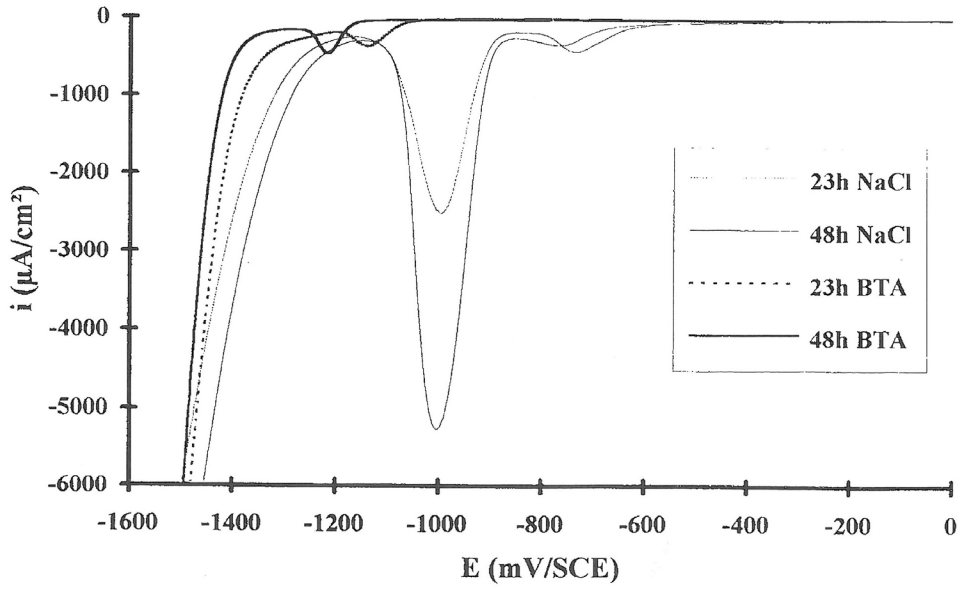

Figure 2. Electrochemical reduction of surface layers formed during 23 and 48 hours in an aerated 0.5M sodium chloride solution with and without BTA (0.1M). Scanning rate, 10 mV.s^{-1}.

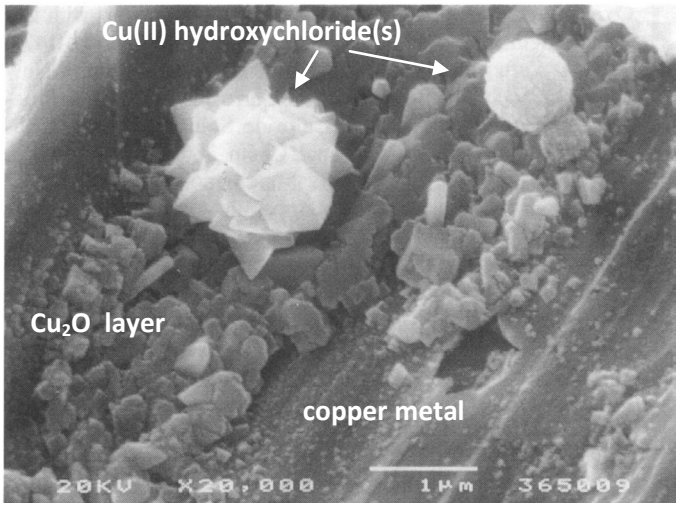

Figure 3. SEM micrograph of cuprous oxide layer on copper formed after 3 days' immersion in an aerated 0.5M sodium chloride solution. White crystals correspond to hydroxychloride compounds $Cu_2(0H)_3Cl$ maybe γ left (paratacamite) and δ right (atacamite).

the reduction peak(s) of Cu_2O is (are) displaced towards still more cathodic values. The thickness of the layer still increases but at a slower rate

SEM analysis

SEM analysis, performed on oxide films formed in a 0.5M NaCl solution during different immersion times, indicate structural modifications of the layer:

- a uniform oxide layer, about 20 nm thickness (as determined by coulometry), is formed during the first four hours of immersion,
- after 72 hours, a discontinuous film, about 160 nm thickness (as determined by coulometry), is formed on the top of the uniform underlayer. This layer probably forms by a redeposition mechanism from soluble Cu(I) or Cu(II) species of the electrolyte,
- after 72 hours of immersion (Figure 3), cupric hydroxychloride $Cu_2(OH)_3Cl$ is identified on top of the Cu_2O layer.

At least two mechanisms of formation can be involved for the growth of the Cu_2O film during immersion of a copper electrode in a NaCl solution. In the first stage of formation, ionic movement through the oxide is the rate determining step for the thickening of a uniform Cu_2O layer. In the second stage, a dissolution - redeposition mechanism can be responsible for the formation of the discontinuous Cu_2O overlayer, leading to a change of the reactivity of the Cu_2O underlayer as observed during the potentiodynamic reduction experiments. In the presence of BTA, only the uniform layer is observed after several days, regardless of the immersion time.

Photoelectrochemical Measurements

Generally, it is admitted that bulk Cu_2O behaves like a p-type semiconductor, characterized by cationic vacancies in the oxide lattice and by the possibility of cationic migration through the film.

Photoelectrochemical measurements are thus a convenient *in situ* method of investigation for the characterization of the conductive properties of the oxide during its growth. An atmospherically formed Cu(I) oxide shows only p-type behaviour, characterized by a cathodic photocurrent under open circuit potential. This p-type of behavior is also described in the literature for bulk Cu_2O and for anodically formed oxides on copper [8-10]. The situation is quite different for oxides obtained by immersion at the open circuit potential in a sodium chloride solution. Figure 4a shows the spectral response of a copper sample after 6 hours immersion in a 0.5M NaCl solution. The photocurrent is initially cathodic in the whole wavelength range under study, indicating a p-type conductivity of the oxide film.

After 66 hours immersion in the same electrolyte (Figure 4b), the photocurrent is still cathodic in the lower wavelength range (0.3-0.4 µm) but becomes anodic in the higher wavelength range (0.4-0.6 µm). Such a behaviour has been attributed [4] to a duplex layer with spatially separated n-type and p-type oxides: Cu_2O with p-type conductivity and cationic vacancies - at the oxide/electrolyte interface; and Cu_2O with n-type conductivity and anionic vacancies or cationic accumulation at the metal/oxide interface.

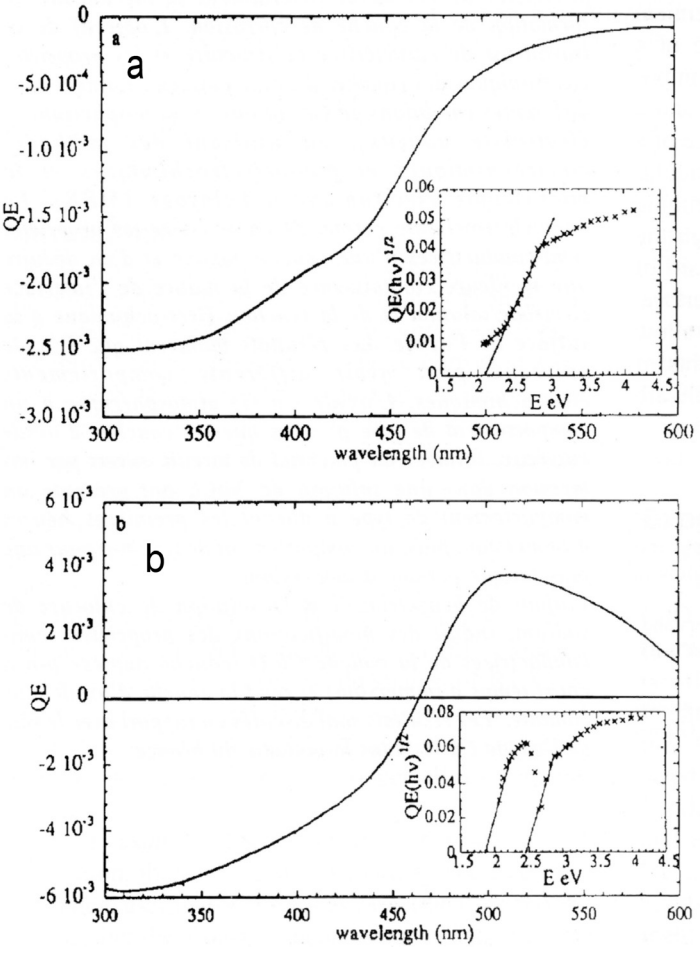

Figure 4 Spectral response of Cu(I) oxide layers formed in a 0.5M NaCl solution after different immersion times: **a:** 6 hours immersion; **b:** 66 hours immersion.

It has been shown [11] that a n-type behaviour appears in the underlayer when a Cu_2O overlayer is deposited from the soluble Cu(I) or Cu(II) species of the electrolyte.

Thus, a duplex oxide layer is characterized by a heterogeneous structure with a gradient of defects throughout the layer. Moreover, an evolution of the degree of non-stoichiometry is possible during the thickening of the film. This evolution results from modification of ionic movements in the oxide and depends on the rate of dissolution/redeposition reactions at the oxide/electrolyte interface.

When BTA is present in the electrolyte, a polymeric (Cu-BTA) layer is expected to form on top of the Cu(I) oxide, hindering the metal dissolution. In this case photoelectrochemical measurements show that a duplex n-p Cu(I) oxide is present from the beginning of the immersion. The accumulation of Cu(I) ions at the metal/oxide interface is then likely to result from the blocking effect of BTA towards copper dissolution.

Conclusion

The differences in the electrochemical reduction curves of naturally grown ox ide layers on copper are evidence of different Cu(I) oxide species with different conducting properties. These properties vary depending on the nature of the electrolyte and on the film preparation conditions.

Different conducting properties in Cu_2O layers have also been shown by photoelectrochemical experiments. In some conditions, the existence of a duplex Cu_2O layer with two semiconducting components of different stoichiometries, *i.e.* a p-type and a n-type component, can be detected. The existence of a n-type Cu_2O at the metal/oxide interface is of particular interest because it offers the possibility for anionic species, such as chloride ions, to diffuse through the oxide. This gives new insight into the mechanism of formation of copper chloride at the metal/oxide interface.

The understanding of this mechanism should allow for better control over the stabilization treatments of chloride containing copper oxide layers which are often observed on ancient copper artefacts.

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Résumé

La corrosion active sur les anciens objets en bronze (maladie du bronze) est liée à la présence de chlorure de cuivre situé sous l'oxyde cuivreux formé à la surface du bronze. Les propriétés de cet oxyde déterminent le mécanisme de formation de la couche de corrosion. L'objectif de ce travail est de caractériser la structure et les propriétés électroniques des couches d'oxyde cuivreux formées sous différentes conditions en circuit ouvert (atmosphérique et électrolyte aqueux), en utilisant des méthodes électrochimiques et photoélectrochimiques et la microscopie électronique à balayage (MEB). La photoélectrochimie permet de caractériser les propriétés semi-conductrices d'une couche passive et d'en déduire une meilleure connaissance de la nature de l'interface électrode/solution et de la réaction électrochimique à la surface de l'oxyde. Les résultats montrent que l'oxyde cuivreux peut avoir différents comportements électrochimiques.

L'oxyde Cu(I) atmosphérique a un comportement de type p, alors que les couches d'oxyde cuivreux, formées au potentiel de circuit ouvert par immersion dans une solution de NaCl, ont présenté un comportement de type p durant les premières heures d'immersion, puis, un comportement de type n-p pour une plus longue période d'immersion.

L'ajout de benzotriazole à la solution de chlorure de sodium, induit des modifications des propriétés semi-conductrices de la couche Cu_2O (couche duplexe p-n à court temps d'immersion) et rend la couche d'oxyde plus isolante. Les résultats sont discutés en rapport avec le rôle de l'oxyde Cu(I) dans la maladie du bronze.